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DETAILED DESCRIPTION

Detailed Description of the Invention]

0001]

[Field of the Invention] This invention relates to the resin constituent which gives the hardened material excellent in still more detailed development nature useful as the solder resist for flexible printed wiring boards, a plating resist, an interlayer insulation film for multilayer printed wiring boards, etc., electric insulation, adhesion, solder thermal resistance, chemical resistance, plating-proof nature, etc., and its hardened material about the photopolymer constituent which used an alkali water-solution fusibility urethane-ized epoxy carboxylate compound (D) and it, and its hardened material.

0002]

[Description of the Prior Art] The liquefied development mold solder resist which carries out image formation and carries out finishing hardening by heat and optical exposure by developing negatives after exposure from a viewpoint of highly precise and high density is used for the noncommercial printed wired board list current [part] by the solder resist of almost all the industrial printed wired board. Moreover, the liquefied solder resist alkali development type [using a dilute alkali water solution as a developer] to consideration of an environmental problem is in use. The solder resist constituent which becomes JP,61-243869,A from a novolak mold epoxy resin, the photopolymer which added the acid anhydride to the resultant of a partial saturation-base acid, a photopolymerization initiator, a diluent, and an epoxy resin, for example an alkali development type solder resist using such a dilute-alkali water solution is indicated.

0003]

[Problem(s) to be Solved by the Invention] High degree of accuracy and densification are called for, aiming at the formation of small lightweight of a pocket device, or improvement in transmission speed, while the demand to a solder resist also serves as **** altitude and maintains flexible nature more rather than the conventional demand in connection with it, the engine performance which can bear substrate adhesion, high insulation, and non-electrolyzed gold plate nature is demanded, and the printed wired board cannot fully respond to these demands in the solder resist by which current marketing is carried out. While the purpose of this invention is excellent in the photosensitivity over an activity energy line and can carry out pattern formation of the detailed image which can respond to the high efficiency of today's printed wired board by development by the dilute-alkali water solution, the hardening film which is made to carry out heat curing and is obtained at a postcure (postcure) process has sufficient flexible nature, and is to offer the resin constituent suitable for the solder resist ink which was excellent in high insulation at adhesion and non-electrolyzed gold plate resistance, and its hardened material.

0004]

[Means for Solving the Problem] this invention persons came to complete this invention wholeheartedly about an alkali water-solution fusibility epoxy carboxylate compound as a result of research in order to solve the above-mentioned technical problem. That is, this invention is [0005]. (1) The alkali water-solution fusibility urethane-ized epoxy carboxylate compound characterized by making the compound (A), compound (B), and compound (C) which are shown below react, and being obtained (D)

Compound A): The epoxy carboxylate compound compound which the epoxy compound (a) which has two epoxy groups in a molecule, and the monocarboxylic-acid compound (b) which has an ethylene nature partial-saturation double bond in a molecule are made to react, and is obtained (B): The carboxylic-acid compound which has two hydroxyl groups in a molecule (B)

Compound (C): Diisocyanate compound.

0006] (2) The weight per epoxy equivalent of an epoxy compound (a) which has two epoxy groups in a molecule An alkali water-solution fusibility urethane-ized epoxy carboxylate compound given in (1) which is a 150-900g [Eq] epoxy compound (D), (3) The epoxy compound (a) which has two epoxy groups in a molecule A phenyl diglycidyl ether

compound, a bisphenol mold epoxy compound, A hydrogenation bisphenol mold epoxy compound, a halogeno-ized isphenol mold epoxy compound, An alicyclic diglycidyl ether compound, an aliphatic series diglycidyl ether compound, 1) which is the epoxy compound chosen from the polysulfide mold diglycidyl ether compound or the biphenol mold epoxy compound, or an alkali water-solution fusibility urethane-ized epoxy carboxylate compound given in any 1 term of 2) (D), (4) The monocarboxylic acid compound (b) which has an ethylene nature partial saturation double bond in a molecule (1) which is monocarboxylic acid chosen from the resultant of an acrylic acid, an acrylic acid (meta), and psilon-caprolactone, or cinnamic acid thru/or an alkali water-solution fusibility urethane-ized epoxy carboxylate compound given in any 1 term of (3) (D), (Meta) (5) The carboxylic-acid compound (B) which has two hydroxyl groups in a molecule (1) which is dimethylol propionic acid or dimethylol butanoic acid thru/or an alkali water-solution fusibility urethane-ized epoxy carboxylate compound given in any 1 term of (4) (D), (6) A diisocyanate compound (C) Phenylene diisocyanate, Tolylene diisocyanate, xylylene diisocyanate, tetramethyl xylylene diisocyanate, Diphenylmethane diisocyanate, naphthalene diisocyanate, TORIDEN diisocyanate, hexamethylene di-isocyanate, dicyclohexylmethane diisocyanate, Isophorone diisocyanate, propine sulfone ether diisocyanate, (1) which is the diisocyanate compound chosen from arylsilane diisocyanate, N-acyl diisocyanate, or lysine diisocyanate thru/or an alkali water-solution fusibility urethane-ized epoxy carboxylate compound given in any 1 term of (5) (D), (7) (1) whose solid content acid number is 50-50 mg-KOH/g thru/or an alkali water-solution fusibility urethane-ized epoxy carboxylate compound given in any 1 term of (6) (D), (8) (1) thru/or an alkali water-solution fusibility urethane-ized epoxy carboxylate compound given in any 1 term of (7) (D), The photopolymer constituent characterized by containing a hardening component (G) as a photopolymerization initiator (E), a cross linking agent (F), and an arbitration component, (9) Hardened material of a photopolymer constituent given in (8) (10) Base material which has the layer of the hardened material of a publication in 9) (11) It is in providing (10) with the goods which have the base material of a publication.

[0007]

[Embodiment of the Invention] The alkali water-solution fusibility urethane-ized epoxy carboxylate compound (D) of this invention is characterized by making a compound (A), an above-mentioned compound (B), and an above-mentioned compound (C) react, and being obtained.

[0008] As for especially the epoxy compound (a) that has two or more epoxy groups in the molecule used in order to manufacture the alkali water-solution fusibility urethane-ized epoxy carboxylate compound (D) of this invention, it is desirable for weight per epoxy equivalent to be a 150-900g [Eq] epoxy compound (a). When a possibility that it may become it is small and difficult to form membranes the molecular weight of the urethane-ized epoxy carboxylate compound (D) obtained when weight per epoxy equivalent is less than 150, and flexible nature may not no longer be obtained enough and weight per epoxy equivalent exceeds 900, there is a possibility that the rate of installation of the monocarboxylic acid (b) which has an ethylene nature partial saturation double bond may become low, and photosensitivity may fall.

[0009] As an example of an epoxy compound of having two epoxy groups in a molecule For example, hydroquinone diglycidyl ether, catechol diglycidyl ether, Phenyl diglycidyl ether, such as resorcinol diglycidyl ether, The bisphenol A mold epoxy resin, a bisphenol-female mold epoxy resin, Bisphenol-smooth S form epoxy resin, 2, and 2-screw (4-hydroxyphenyl) - Bisphenol mold epoxy compounds, such as an epoxy compound of 1, 1, 1, 3, 3, and 3-hexafluoropropane, A hydrogenation bisphenol A mold epoxy resin, a hydrogenation bisphenol-female mold epoxy resin, a hydrogenation bisphenol-smooth S form epoxy resin, hydrogenation 2, 2-screw (4-hydroxyphenyl) - Hydrogenation bisphenol mold epoxy compounds, such as an epoxy compound of 1, 1, 1, 3, 3, and 3-hexafluoropropane, Halogeno-ized bisphenol mold epoxy compounds, such as a bromination bisphenol A mold epoxy resin and a bromination bisphenol-female mold epoxy resin, Alicyclic diglycidyl ether compounds, such as a cyclohexane dimethanol diglycidyl ether compound, 1, 6-hexanediol diglycidyl ether, 1,4-butanediol diglycidyl ether, Polysulfide mold diglycidyl ether compounds, such as aliphatic series diglycidyl ether compounds, such as diethylene-glycol diglycidyl ether, and polysulfide diglycidyl ether, a biphenol mold epoxy resin, etc. are mentioned.

[0010] As a commercial item of these epoxy compounds, for example Epicoat 828, Epicoat 1001, Epicoat 1002, Epicoat 1003, Epicoat 1004 (all are the products made from Japan epoxy resin), EPO MIKKU R-140, EPO MIKKU R-301, EPO MIKKU R-304 (all are the Mitsui Chemicals make), DER-331, DER-332, DER-324 (all are the Dow Chemical Co. make), Epiclone 840, Epiclone 850 (all are Dainippon Ink make) UVR-6410 (made in Union Carbide), The bisphenol A mold epoxy resins, such as YD-8125 (Tohto Kasei Co., Ltd. make), UVR-6490 (made in Union Carbide), YDF-2001, YDF-2004, YDF-8170 (all are the Tohto Kasei Co., Ltd. make), Bisphenol-female mold epoxy resins, such as Epiclone 30 and Epiclone 835 (all are the Dainippon Ink make), Hydrogenation bisphenol A mold epoxy resins, such as HBPAGE (Maruzen Petrochemical make) and RIKAREJIN HBE-100 (New Japan Chemical make), Bromination bisphenol A mold epoxy resins, such as DER-513, DER-514, and DER-542 (all are the Dow Chemical Co. make), The SEROKI side

021 (product made from a die cel), RIKAREJIN DME-100 (New Japan Chemical make), Cycloaliphatic epoxy resin, such as EX-216 (Nagase Brothers formation make), ED-503 (product made from the Asahi electrification), Aliphatic series diglycidyl ether compounds, such as RIKAREJIN W-100 (New Japan Chemical make), EX-212, EX-214, and EX-50 (all Nagase Brothers formation make), Biphenol mold epoxy compounds, such as polysulfide mold diglycidyl ether compounds, such as FLEP-50 and FLEP-60 (all are the products made from the Toray Industries thiokol), and YX-4000 (product made from Japan epoxy resin), are mentioned.

0011] As a monocarboxylic acid compound (b) which has an ethylene nature partial saturation double bond, the reactant of acrylic acids, a crotonic acid, alpha-cyano cinnamic acid, cinnamic acid, saturation or a partial saturation dibasic acid, and a partial saturation radical content monoglycidyl compound is mentioned, for example into the molecule used in order to manufacture the alkali water-solution fusibility urethane-ized epoxy carboxylate compound (D) of this invention. As acrylic acids, for example (meta) An acrylic acid, beta-styryl acrylic acid, The half-ester which are beta-furfuryl acrylic acid, saturation or a partial saturation dibasic-acid anhydride, the acrylate derivative that has one hydroxyl group in 1 molecule (meta), and this mol reactant Although the half-ester which is this mol reactant of saturation or a partial saturation dibasic acid, and monoglycidyl (meta) acrylate derivatives is mentioned Especially the resultant or cinnamic acid of an acrylic acid (meta), an acrylic acid (meta), and epsilon-caprolactone is desirable in respect of the sensibility when considering as a photopolymer constituent.

0012] Although all can be used if it is the compound which has an alcoholic hydroxyl group, and/or a phenolic hydroxyl group and a carboxyl group in a molecule at coincidence as a carboxylic-acid compound (B) which has two hydroxyl groups in the molecule used in order to manufacture the alkali water-solution fusibility urethane-ized epoxy carboxylate compound (D) of this invention, dimethylol propionic acid or dimethylol butanoic acid excellent in especially alkali water-solution development nature etc. is desirable.

0013] Although all can be used as a diisocyanate compound (C) used in order to manufacture the alkali water-solution fusibility urethane-ized epoxy carboxylate compound (D) of this invention if it has two isocyanate radicals in a molecule phenylene diisocyanate, tolylene diisocyanate excellent in especially flexibility etc., Xylylene diisocyanate, tetramethyl xylylene diisocyanate, Diphenylmethane diisocyanate, naphthalene diisocyanate, TORIDEN diisocyanate, hexamethylene diisocyanate, dicyclohexylmethane diisocyanate, Isophorone diisocyanate, propine sulfone ether diisocyanate, arylsilane diisocyanate, N-acyl diisocyanate, or lysine diisocyanate is desirable.

0014] Manufacture of the alkali water-solution fusibility urethane-ized epoxy carboxylate compound (D) of this invention the epoxy carboxylate compound (A) which the alcoholic hydroxyl group generated by the reaction (henceforth the first reaction) of the above-mentioned epoxy compound (a) and the monocarboxylic acid compound (b) which has an ethylene nature partial saturation double bond in a molecule -- and [0015] which can carry out the urethane-ized reaction henceforth the second reaction) of the carboxylic-acid compound (B) which has two hydroxyl groups, and can obtain it with a diisocyanate compound (C) in a molecule On the solvent and concrete target which do not have a non-solvent or alcoholic hydroxyl group, the first reaction for example Ketones, such as an acetone, ethyl methyl ketone, and a cyclohexanone, benzene, Aromatic hydrocarbon, such as toluene, a xylene, and tetramethyl benzene Ethylene glycol wood ether, ethylene glycol diethylether, Dipropylene glycol wood ether, dipropylene glycol diethylether, Glycol ether, such as triethylene glycol wood ether and triethylene glycol diethylether Ethyl acetate, butyl acetate, methyl-cellosolve acetate, ethylcellosolve acetate, Butyl-cellosolve acetate, carbitol acetate, propylene-glycol-monomethyl-ether acetate, ester, such as glutaric-acid dialkyl, succinic-acid dialkyl, and dialkyl adipate It can carry out in independent or mixed organic solvents, such as petroleum solvents, such as cyclic ester, such as gamma-butyrolactone, the petroleum ether, petroleum naphtha, hydrogenation petroleum naphtha, and solvent naphtha, and a cross linking agent (F) mentioned further later.

0016] the raw material in this reaction teaches -- as the monocarboxylic acid compound (b) which has an ethylene nature partial saturation double bond in a molecule in a molecule if it carries out comparatively -- an epoxy compound (a) -- it is desirable that 80-120Eq is % to 1Eq. When it deviates from this range, since there are a possibility of causing gelation during the second reaction, and a possibility that the thermal stability of an alkali water-solution fusibility urethane-ized epoxy carboxylate compound (D) finally obtained may become low, it is not desirable.

0017] In order to make reaction time promote a reaction, it is desirable to use a catalyst and the amount of this catalyst used is 0.1 - 10 % of the weight to a reactant. The reaction temperature in that case is 60-150 degrees C, and reaction time is 5 - 60 hours preferably. As an example of the catalyst to be used, triethylamine, benzyl dimethylamine, triethyl ammoniumchloride, a benzyl trimethylammonium star's picture, benzyl trimethylammonium iodide, triphenylphosphine, triphenyl stibine, a methyl triphenyl stibine, octanoic-acid chromium, an octanoic-acid zirconium, etc. are mentioned, for example.

0018] After the first reaction termination, after the second reaction's adding the carboxylic-acid compound (B) which has

two hydroxyl groups to reaction mixture and using it as dispersion liquid or a solution into the above-mentioned molecule, it is an urethane-ized reaction to which add the further above-mentioned diisocyanate compound (C) gradually, and it is made to react. In order to promote a reaction, a catalyst can also be used, it can react with a non-catalyst and the amount of this catalyst used is 0.01 - 10 % of the weight to a reactant. As reaction temperature in this case, it is 40-120 degrees C, and reaction time is 5 - 60 hours preferably.

[2019] In the charge of each component, as a carboxylic-acid compound (B) which has two hydroxyl groups in a molecular weight calculated value from which the solid content acid number of the alkali water-solution fusibility urethane-ized epoxy carboxylate compound (D) of this invention serves as 50 - 150 mg-KOH/g is added. as a diisocyanate compound (C) -- (the mol of a compound (A) -- the mol of a number + compound (B) -- it is desirable to teach so that number)/(mol of compound C number) may become the range of 1-5. Since there is a possibility that an isocyanate radical will remain at this value, the case of less than one at the end of the alkali water-solution fusibility urethane-ized epoxy carboxylate compound (D) of this invention, and thermal stability may gel during preservation low, it is not desirable. Moreover, when this value exceeds 5, the molecular weight of an alkali water-solution fusibility urethane-ized epoxy carboxylate compound (D) becomes low, and there is a possibility that the problem of tack nature and the problem of low sensibility may arise. Moreover, when the solid content acid number is less than 50 mg-KOH/g, the solubility over an alkali water solution is inadequate, and a possibility of remaining as residue, and when the worst [patterning is performed, and], there is a possibility that patterning may become impossible. Moreover, it is [fear of the solubility over an alkali water solution becoming high too much, and the pattern which carried out photo-curing exfoliating] and is not desirable when the solid content acid number exceeds 150 mg-KOH/g.

[2020] The photopolymer constituent of this invention is characterized by containing a hardening component (G) as the above-mentioned alkali water-solution fusibility urethane-ized epoxy carboxylate compound (D) and a photopolymerization-initiator (E), a cross linking agent (F), and an arbitration component.

[2021] As a content rate of the above-mentioned alkali water-solution fusibility urethane-ized epoxy carboxylate compound (D) used for the photopolymer constituent of this invention, when solid content of a photopolymer constituent is made into 100 % of the weight, it is usually 20 - 60 % of the weight preferably 15 to 70% of the weight.

[2022] As an example of the photopolymerization initiator (E) used for the photopolymer constituent of this invention For example, a benzoin, benzoin methyl ether, benzoin ethyl ether, Benzoin, such as the benzoin propyl ether and benzoin isobutyl ether; An acetophenone, A 2 and 2-diethoxy-2-phenyl acetophenone, 2, and 2-diethoxy-2-phenyl acetophenone, and 1-dichloro acetophenone, 2 - Hydroxy-2-methyl-phenyl propane-1-ON, A diethoxy acetophenone, 1-hydroxyine cloxyl phenyl ketone, Acetophenones, such as 2-methyl-1-[4-(methylthio) phenyl]-2-morpholino propane-1-ON; 2-ethyl anthraquinone, 2-tertiary butyl anthraquinone, 2-chloro anthraquinone, Anthraquinone, such as 2-amyl anthraquinone; 2, 2-diethylthio xanthone, Thioxan tons, such as 2-isopropyl thioxan ton and 2-chloro thioxan ton; Acetophenone dimethyl acetal, Ketals, such as benzyl dimethyl ketal; A benzophenone, 4-benzoyl-4'-methyl diphenyl sulfide, Benzophenones, such as a 4 and 4'-screw methylamino benzophenone; phosphine oxide, such as 2, 4, 6-trimethyl benzoyl diphenylphosphine oxide, and bis(2, 4, 6-trimethyl benzoyl)-phenyl phosphine oxide, is mentioned. As these addition rates, when solid content of a photopolymer constituent is made into 100 % of the weight, it is usually 2 - 25 % of the weight preferably one to 30% of the weight.

[2023] These can be used as independent or two or more sorts of mixture, and can be further used combining accelerators such as benzoic-acid derivatives, such as tertiary amine [, such as triethanolamine and methyldiethanolamine,], N, and N-dimethylamino ethyl benzoate ester, N, and N-dimethylamino isoamyl benzoate ester, etc. As an addition of these accelerators, 100% or less of addition is desirable to a photopolymerization initiator (E).

[2024] As an example of the cross linking agent (F) used for the photopolymer constituent of this invention For example, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, 1,4-butanediol monochrome (meta) acrylate, carbitol (meta) acrylate, Acryloyl morpholine, hydroxyl-group content (meta) acrylate for example, 2-hydroxyethyl (meta) acrylate and 2-hydroxypropyl (meta) acrylate -- The acid anhydride of 1,4-butanediol monochrome (meta) acrylate etc. and a polycarboxylic acid compound for example, a non-succinic acid, a maleic anhydride, phthalic anhydride, and tetrahydro phthalic anhydride -- Half ester, Pori ethylene glycol di(meth)acrylate which are reactants, such as hexahydro phthalic anhydride, Tori propyleneglycol di(meth) acrylate, TORIMECHI roll pro pantry (meta) acrylate, Trimethylol propane PORIETOKISHITORI (meta) acrylate, GURISEN polypropylene POKISHITORI (meta) acrylate, The di(meth) acrylate of epsilon-caprolactone addition product of a hydronalium KISHIBI valine acid neo pen glycol For example, (the Lippon Kayaku Co., Ltd. make, KAYARAD HX-220, HX-620), etc., Pentaerythritol tetrapod (meta) acrylate, the Pori (meta) acrylate of the reactant of dipentaerythritol and epsilon-caprolactone, Dipentaerythritol poly (meta) acrylate, monochrome, or a poly glycidyl compound for example, butyl glycidyl ether and phenyl glycidyl ether -- Polyethylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, 1, 6-hexanediol diglycidyl ether, diglycidyl

exahydrophthalate, Glycerol poly glycidyl ether, glycerol poly ethoxy glycidyl ether, The epoxy (meta) acrylate which is dimethylolpropane polyglycidyl ether, trimethylol propane PORIETOKISHI poly glycidyl ether, etc. and the reactant of an acrylic acid (meta) can be mentioned. As these addition rates, when solid content of a photopolymer constituent is made into 100 % of the weight, it is usually 5 - 30 % of the weight preferably two to 40% of the weight.

[0225] As for the hardening component (G) as an arbitration component used for the photopolymer constituent of this invention, an epoxy compound, an oxazine compound, etc. are mentioned. A hardening component (G) reacts with the carboxyl group and heating which remain in the resin paint film after photo-curing, and when it is going to obtain the hardening paint film which has still firmer chemical resistance, it is used especially preferably.

[0226] As an example of the epoxy compound used for a hardening component (G), for example, a phenol novolak mold epoxy resin, a cresol novolak mold epoxy resin, a tris hydroxyphenyl methane mold epoxy resin, a dicyclopentadiene phenol mold epoxy resin, the bisphenol A mold epoxy resin, a bisphenol-female mold epoxy resin, a biphenol mold epoxy resin, a bisphenol-A novolak mold epoxy resin, a naphthalene frame content epoxy resin, a heterocycle type epoxy resin, etc. are mentioned.

[0227] As a phenol novolak mold epoxy resin, Epiclone N-770 (Dainippon Ink & Chemicals, Inc. make), D.E.N438 (Dow Chemical Co. make), Epicoat 154 (product made from oil-ized Shell Epoxy), RE-306 (Nippon Kayaku Co., Ltd. make), etc. are mentioned, for example. As a cresol novolak mold epoxy resin, Epiclone N-695 (Dainippon Ink & Chemicals, Inc. make), EOCN-102S, EOCN-103S, EOCN-104S (Nippon Kayaku Co., Ltd. make), UVR-6650 (made in Union Carbide), EOCN-195 (Sumitomo Chemical Co., Ltd. make), etc. are mentioned, for example.

[0228] As a tris hydroxyphenyl methane mold epoxy resin, EPPN-503, EPPN-502H, EPPN-501H (Nippon Kayaku Co., Ltd. make), TACTIX-742 (Dow Chemical Co. make), Epicoat E1032H60 (product made from oil-ized Shell Epoxy), etc. are mentioned, for example. As a dicyclopentadiene phenol mold epoxy resin, Epiclone EXA-7200 (Dainippon Ink & Chemicals, Inc. make), TACTIX-556 (Dow Chemical Co. make), etc. are mentioned, for example.

[0229] As a bisphenol mold epoxy resin, bisphenol-female mold epoxy resins, such as the bisphenol A mold epoxy resins such as Epicoat 828, Epicoat 1001 (product made from oil-ized shell epoxy), UVR-6410 (made in Union Carbide), D.E.R. 31 (Dow Chemical Co. make), and YD-8125 (Tohto Kasei Co., Ltd. make), UVR-6490 (made in Union Carbide), and YD-8170 (Tohto Kasei Co., Ltd. make), etc. are mentioned, for example.

[0230] As a biphenol mold epoxy resin, biphenol mold epoxy resins, such as NC-3000P and NC-3000S (Nippon Kayaku Co., Ltd. nature), the BIKISHIRE Norian mold epoxy resin of YX-4000 (product made from oil-ized Shell Epoxy), YL-121 (product made from oil-ized Shell Epoxy), etc. are mentioned, for example. As a bisphenol A novolak mold epoxy resin, Epiclone N-880 (Dainippon Ink & Chemicals, Inc. make), Epicoat E157S75 (product made from oil-ized Shell Epoxy), etc. are mentioned, for example.

[0231] As a naphthalene frame content epoxy resin, NC-7000 (Nippon Kayaku Co., Ltd. make), EXA-4750 (Dainippon Ink & Chemicals, Inc. make), etc. are mentioned, for example. As cycloaliphatic epoxy resin, EHPE-3150 (Daicel Chemical Industries, Ltd. make) etc. is mentioned, for example. As a heterocycle type epoxy resin, TEPIK, TEPIK-L, TEPIK-H, TEPIK-S (all are the Nissan Chemical Industries, Ltd. make), etc. are mentioned, for example.

[0232] Hardening component (G) As an example of the oxazine compound used, for example, B-m mold benzoxazine, P-mold benzoxazine, and B-a mold benzoxazine (all are the Shikoku Chemicals Corp. make) are mentioned.

[0233] As an addition rate of a hardening component (G), 200% or less of amount of the equivalent calculated from the solid content acid number and the amount of an alkali water-solution fusibility epoxy carboxylate compound of this invention used is desirable. It is [a possibility that the development nature of the photopolymer constituent of this invention may fall remarkably] and is not desirable if this amount exceeds 200%.

[0234] further -- the need -- responding -- thixotropy grant agents, such as bulking agents, such as various kinds of additives, for example, talc, a barium sulfate, a calcium carbonate, a magnesium carbonate, barium titanate, an aluminum hydroxide, an aluminum oxide, a silica, and clay, and Aerosil, -- polymerization inhibitor, such as a leveling agent of coloring agents, such as; copper phthalocyanine blue, Phthalocyanine Green, and titanium oxide, silicone, and a fluorine system, and defoaming agent; hydroquinone, the hydroquinone monomethyl ether, etc. can be added in order to raise many engine performance of a constituent.

[0235] In addition, although you may mix to the above and a resin constituent beforehand, it can mix and the above-mentioned hardening component (G) can also be used, before spreading to a printed wired board. That is, it is desirable to make the above and the (A) component into a subject, to blend with the 2 liquid type of the base resin solution which blended the epoxy hardening accelerator etc. with this, and the curing agent solution which made the aforementioned (D) component the subject, and to mix and use these on the occasion of use.

[0236] The photopolymer constituent of this invention can also be used as a photographic sensitive film applied as a base material for example, on the polymer film (for example, film which consists of polyethylene terephthalate, polypropylene

olyethylene, etc.).

0037] It is useful as the insulating material between the layers of electronic parts, and resist ink, such as a solder resist for printed circuit boards, and also the photopolymer constituent (the shape of liquefied or a film) of this invention can be used as printing ink, a **** agent, a coating, a coating agent, adhesives, etc.

0038] The hardened material of this invention stiffens the resin constituent of above-mentioned this invention by the energy-line exposure of ultraviolet rays etc. Hardening can be performed with a conventional method by the energy-line exposure of ultraviolet rays etc. For example, what is necessary is just to use ultraviolet-rays generators, such as a low pressure mercury lamp, a high pressure mercury vapor lamp, an ultrahigh pressure mercury lamp, a xenon LGT, and ultraviolet-rays luminescence laser (excimer laser etc.), when irradiating ultraviolet rays. The hardened material of the resin constituent of this invention is used for the electrical and electric equipment and electronic parts like a printed circuit board as layer insulation material for a permanent resist or build up methods of construction. The thickness of this hardened material layer has desirable about 1-60 micrometers at about 0.5-160 micrometers.

0039] The printed wired board of this invention can be obtained as follows, for example. That is, when using a liquefied resin constituent, a paint film can be formed by applying the constituent of this invention to the substrate for printed circuits by 5-160-micrometer thickness by approaches, such as screen printing, a spray method, the roll coat method, electrostatic spray painting, and the curtain coat method, and making it usually dry preferably 60-110 degrees C of paint films with the degree of ** of 60-100 degrees C. Then, the photo mask in which exposure patterns, such as a negative film, were formed is directly contacted to a paint film (or it places on a paint film in the condition of not contacting), ultraviolet rays are usually irradiated by about two 10 - 2000 mJ/cm strength, and negatives are developed by the spray, rocking immersion, brushing, scrubbing, etc., using the developer which mentions a part for an unexposed part later. Then, ultraviolet rays are irradiated further if needed, subsequently, by heat-treating at the temperature of 140-180 degree C preferably, it excels in gold plate nature and 100-200 degrees C of printed wired boards which have the permanent protective coat with which are satisfied of many properties, such as thermal resistance, solvent resistance, acid resistance, adhesion, and flexibility, are usually obtained.

0040] As an alkali water solution used for the above and development, organic alkali water solutions, such as inorganic alkali water solutions, such as a potassium hydroxide, a sodium hydroxide, a sodium carbonate, potassium carbonate, a sodium hydrogencarbonate, a potassium hydrogencarbonate, sodium phosphate, and potassium phosphate, tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide, monoethanolamine, diethanolamine, and triethanolamine, can be used.

0041]

Example] Hereafter, although an example explains this invention still more concretely, this invention is not limited to the following example.

0042] As an epoxy compound (a) which has two or more epoxy groups in a molecule in 2L flask which attached example stirring equipment and reflux tubing Mitsui Chemicals make [] -- EP-807 (a 2 organic-functions bisphenol-female mold epoxy resin --) An acrylic acid (molecular weight: 72.06) as a monocarboxylic acid compound (b) which has an ethylene nature partial saturation double bond in 340.0g and a molecule in 170g/Eq Weight per epoxy equivalent : 144.1g, Teach 2-methyl hydroquinone as thermal polymerization inhibitor, and 1.45g of triphenylphosphines is taught as 0.24g and a reaction catalyst. It was made to react until the acid number of reaction mixture became 0.5 or less mg-KOH/g at the temperature of 98 degrees C, and an epoxy carboxylate compound (A) and (theoretical molecular weight:484.1) were obtained. Subsequently, the 2 and 2-bis(dimethylol)-propionic acid (molecular weight: 134.16) was added as a carboxylic acid compound (B) which has 360.2g in this reaction mixture, and has two hydroxyl groups for carbitol acetate in a molecule as a solvent for a reaction, 0.60g of 2-methyl hydroquinone was added as 134.1g and thermal polymerization inhibitor, and the temperature up was carried out to 60 degrees C. Isophorone diisocyanate (molecular weight: 222.3) 22.3g was gradually dropped at this solution so that reaction temperature might not exceed 65 degrees C. Carry out the temperature up of the temperature to 80 degrees C after dropping termination, it is made to react with infrared absorption spectrometry for 6 hours until absorption near 2250 kaysers is lost, and it is the alkali water-solution fusibility urethane-ized epoxy carboxylate compound of this invention. The resin solution containing 70 % of the weight was obtained (this solution is set to D-1). When the solid content acid number was measured, it was 66 mg-KOH/g.

0043] As an epoxy compound (a) which has two or more epoxy groups in a molecule in 2L flask which attached example stirring equipment and reflux tubing Epicoat 828 (2 organic-functions bisphenol A mold epoxy resin --) made fromapan epoxy resin An acrylic acid (molecular weight: 72.06) as a monocarboxylic acid compound (b) which has an ethylene nature partial saturation double bond in 366.0g and a molecule in 183g/Eq Weight per epoxy equivalent : 144.1g Teach 2-methyl hydroquinone as thermal polymerization inhibitor, and 1.56g of triphenylphosphines is taught as 0.26g and a reaction catalyst. It was made to react until the acid number of reaction mixture became 0.5 or less mg-KOH/g at th

temperature of 98 degrees C, and an epoxy carboxylate compound (A) and (theoretical molecular weight: 510.1) were obtained. Subsequently, the 2 and 2-bis(dimethylol)-propionic acid (molecular weight: 134.16) was added as a carboxylic acid compound (B) which has 296.9g in this reaction mixture, and has two hydroxyl groups for carbitol acetate in a molecule as a solvent for a reaction, 0.64g of 2-methyl hydroquinone was added as 182.6g and thermal polymerization inhibitor, and the temperature up was carried out to 50 degrees C. The solution which dissolved tolylene diisocyanate (molecular weight: 174.2) 205.5g in this solution at carbitol acetate 88.0g was gradually dropped so that reaction temperature might not exceed 55 degrees C. Carry out the temperature up of the temperature to 80 degrees C after stopping termination, it is made to react with infrared absorption spectrometry for 6 hours until absorption near 2250 cm⁻¹ is lost, and it is the alkali water-solution fusibility urethane-ized epoxy carboxylate compound of this invention. The resin solution containing 70 % of the weight was obtained (this solution is set to D-2). When the solid content acid number was measured, it was 85 mg-KOH/g.

[0044] As an epoxy compound (a) which has two or more epoxy groups in a molecule in 3L flask which attached example stirring equipment and reflux tubing Flep -60 (2 organic-functions mold polysulfide mold epoxy resin --) made from the Toray Industries thiokol An acrylic acid (molecular weight: 72.06) as a monocarboxylic acid compound (b) which has an ethylene nature partial saturation double bond in 576g and a molecule in 288g/Eq Weight per epoxy equivalent : 144.1g, brought 0.36g of 2-methyl hydroquinone as thermal polymerization inhibitor, it was made to react until the acid number of reaction mixture became 0.5 or less mg-KOH/g at the temperature of 98 degrees C, and an epoxy carboxylate compound (A) and (theoretical molecular weight: 720.1) were obtained. Subsequently, the 2 and 2-bis(dimethylol)-propionic acid (molecular weight: 134.16) was added as a carboxylic-acid compound (B) which has 622.9g in this reaction mixture, and as two hydroxyl groups for carbitol acetate in a molecule as a solvent for a reaction, 1.04g of 2-methyl hydroquinone was added as 278.0g and thermal polymerization inhibitor, and the temperature up was carried out to 60 degrees C. Diphenylmethane diisocyanate (molecular weight: 222.3) 455.3g was gradually dropped at this solution so that reaction temperature might not exceed 65 degrees C. Carry out the temperature up of the temperature to 80 degrees C after stopping termination, it is made to react with infrared absorption spectrometry for 6 hours until absorption near 2250 cm⁻¹ is lost, and it is the alkali water-solution fusibility urethane-ized epoxy carboxylate compound of this invention. The resin solution containing 70 % of the weight was obtained (this solution is set to D-3). When the solid content acid number was measured, it was 80 mg-KOH/g.

[0045] the inside of 1L flask which attached comparison resin composition stirring equipment and reflux tubing -- Nippon Kayaku make [] -- EOCN-104S (a polyfunctional cresol novolak mold epoxy resin --) Carbitol acetate as 72.1g and a solvent for a reaction for 220g and an acrylic acid in 220g/Eq Weight per epoxy equivalent : as 125.2g and thermal polymerization inhibitor Triphenylphosphine 1.25g was added by having made 2-methyl hydroquinone into 0.21g and a reaction catalyst, and it was made to react at the temperature of 98 degrees C for 24 hours. Subsequently, added 105.7g of carbitol acetate for RIKASHIDDO TH (New Japan Chemical tetrahydro phthalic anhydride), added 0.28g for 45.3g of 2-methyl hydroquinone to this reaction mixture, it was made to react at the temperature of 95 degrees C for 4 hours, and the comparison resin of 70% of solid content concentration and solid content acid-number 98 mg-KOH/g was obtained.

[0046] It kneaded by 3 roll mills mixing and if needed by (D-2) and (D-3) the blending ratio of coal which shows comparison resin in Table 1 obtained in examples 4-6 and the example of comparison 1 aforementioned examples 1-3 (D-1), and the photopolymer constituent of this invention was obtained. With screen printing, this was applied to the printed circuit board so that it might become the thickness whose desiccation thickness is 15-25 micrometers, and the paint film was dried with the 80-degree C air forced oven for 30 minutes. Subsequently, ultraviolet rays were irradiated through the mask with which the circuit pattern was drawn using the ultraviolet-rays aligner (ORC Manufacturing Co., Ltd., form IMW-680GW). Then, the sodium-carbonate water solution performed spray development 1%, and the resin of the ultraviolet-rays the non-irradiated section was removed. After carrying out rinsing desiccation, the heat hardening reaction of the printed circuit board was carried out with the 150-degree C air forced oven for 60 minutes, and the hardening film was obtained. About the obtained hardened material, the trial of photosensitivity, surface gloss, substrate camber, flexibility, adhesion, a pencil degree of hardness, solvent resistance, acid resistance, thermal resistance, and gold plate-roof nature was performed as below-mentioned. Those results are shown in Table 2. In addition, a test method and the valuation approach are as follows.

[0047] (Development nature) The following valuation basis was used.

1) At the time of development, ink was removed completely and negatives have been developed.

2) There is a part which is not developed at the time of development.

[0048] (Definition) A 50-micrometer negative pattern is stuck to the paint film after desiccation, and exposure exposure of the ultraviolet rays of addition quantity of light 200 mJ/cm² is carried out. Next, negatives are developed with the spray

pressure of 2.0kg/cm² for 60 seconds in 1% of sodium-carbonate water solution, and an imprint pattern is observed under microscope. The following criteria were used.

) In a straight line, the pattern edge is resolved.

.... Exfoliation or a pattern edge is notched.

0049] (Photosensitivity) 21 steps (product made from KODAKKU) of step tablets are stuck to the paint film after desiccation, and it is addition quantity of light 500 mJ/cm². Exposure exposure of the ultraviolet rays is carried out. Next, they are for 60 seconds and 2.0kg/cm² with 1% of sodium-carbonate water solution. Negatives are developed with spray pressure and the number of stages of the paint film which remained without developing negatives is checked.

0050] (Surface gloss) To the paint film after desiccation, it is 500 mJ/cm². Exposure exposure of the ultraviolet rays is carried out. Next, negatives are developed with the spray pressure of 2.0kg/cm² for 60 seconds in 1% of sodium-carbonate water solution, and the hardening film after desiccation is observed. The following criteria were used.

) x as which cloudiness is not regarded at all [0051] as which some cloudiness is regarded (Substrate camber) The following criteria were used.

) It is ** as which camber is not regarded by the substrate.... It is x which the substrate is meeting very only.... It is 0052] as which the camber of a substrate is regarded. (Flexibility) The hardening film is bent and observed at 180 degrees C. The following criteria were used.

) It is x as which a crack is not regarded by the film surface.... It is [0053] into which a film surface is divided.

Adhesion) JIS According to K5400, the 100 piece making-Scotch tape (R) performed the peeling trial for eye 1mm **** the test piece. The desquamative state of eye **** was observed and the following criteria estimated.

) Thing x without peeling What exfoliating [0054] (Pencil degree of hardness) JIS It evaluated according to 5400.

0055] (Solvent resistance) A test piece is immersed in isopropyl alcohol for 30 minutes at a room temperature. After checking whether there are any abnormalities in an appearance, the peeling trial by the Scotch tape (R) was performed, and the following criteria estimated.

) Thing x which does not have abnormalities in a paint film appearance and has neither blistering nor exfoliation

What has blistering and exfoliation in a paint film [0056] (Acid resistance) A test piece is immersed in a hydrochloric-acid water solution at a room temperature 10% for 30 minutes. After checking whether there are any abnormalities in an appearance, the peeling trial by the Scotch tape (R) was performed, and the following criteria estimated.

) Thing x which does not have abnormalities in a paint film appearance and has neither blistering nor exfoliation

What has blistering and exfoliation in a paint film [0057] (Thermal resistance) Rosin system PURAKKUSU was applied to the test piece, and it was immersed in the 260-degree C solder tub for 5 seconds. This is made into 1 cycle and it is 3 cycle *****. After cooling radiationally to a room temperature, the peeling trial by the Scotch tape (R) was performed, and the following criteria estimated.

) Thing x which does not have abnormalities in a paint film appearance and has neither blistering nor exfoliation

What has blistering and exfoliation in a paint film [0058] (Gold plate-proof nature) after it rinses a trial substrate after being immersed in 30-degree C acid cleaning liquid (the product made from a Japanese MAKUDA mitt, 20vol% water solution of Metex L-5B) for 3 minutes, and being immersed for 3 minutes at a room temperature subsequently to a 4.4wt% ammonium-persulfate water solution -- rinsing -- further -- after the trial substrate was immersed in the 10vol% sulfuric-acid water solution for 1 minute at the room temperature, it rinsed. Next, it was immersed in 30-degree C catalytic liquid (10vol% water solution of the Meltex make and the metal plate activator 350) for 7 minutes, and this substrate was rinsed, and after being immersed in 85-degree C nickel-plating liquid (the Meltex make, the 20vol% water solution of mel plate nickel-865M, pH4.6) for 20 minutes and performing nickel plating, in the 10vol% sulfuric-acid water solution, at the room temperature, it was immersed for 1 minute and rinsed. Subsequently, after immersing the trial substrate in 95-degree C liquid gilding (the Meltex make, a water solution (OUROREKUTORO loess UP15vol% and old cyanide potassium 3vol%), pH6) for 10 minutes and performing non-electrolyzed gold plate, it rinsed, and with 60 more-degree C warm water, it was immersed for 3 minutes, rinsed and dried. The condition when adhering and exfoliating cellophane adhesive tape in the obtained non-electrolyzed gold plate evaluation substrate was observed.

) : that which is completely normal.

: What peeling was regarded as a little.

0059] (PCT-proof nature) After checking whether there are any abnormalities in an appearance after 96-hour neglect about a trial substrate underwater [of 121 degrees C and two atmospheric pressures], the peeling trial by the Scotch tape (R) was performed, and the following criteria estimated.

) Thing x which does not have abnormalities in a paint film appearance and has neither blistering nor exfoliation

What has blistering and exfoliation in a paint film [0060] (Thermal shock resistance) 125 degrees C / 30 minutes were

made into 1 cycle for the test piece for -55 degrees C / 30 minutes, the heat history was added, microscope observation of the test piece was carried out after 1000 cycle progress, and the following criteria estimated.

.... Thing x which does not have generating of a crack in a paint film What the crack generated in the paint film

0061]

Table 1 [] An example The example of a comparison Notes 4 5 6 One resin solution D-1 43.14 D-2 43.14 D-3 43.14 43.14

cross linking agents (F)

PCA-60 *1 7.05 7.05 DPHA *2 7.05 7.05 photopolymerization initiator (E)

RGACURE 907 *3 7.05 7.05 7.05 7.05 DETX-S *4 0.70 0.70 0.70 0.70 hardening components (G)

X-4000 * 5 12.08 12.08 12.08 12.08 heat-curing catalyst Melamine 1.01 1.01 1.01 1.01 fillers Barium sulfate 15.00

5.00 15.00 15.00 Copper phthalocyanine blue 0.50 0.50 0.50 0.50 additives BYK-354 *6 0.70 0.70 0.70 0.70 KS-66 *7

0.700.70 0.700.70 solvent CA 12.0612.06 12.06 12.06 [0062] notes *1 trimethylolpropane triacrylate -- :2Made from *3

antico-methyl-(4-(methylthio) phenyl)- 2-morpholino-1-propane *4 Nippon Kayaku make [] -- product [] made from :

and 4-diethylthio xanthone *5 JER -- :2 organic-functions biphenyl frame epoxy resin *6 [] -- Made from : leveling agent

7 made from big KEMI Shin-etsu chemistry: -- defoaming agent Nippon Kayaku make : epsilon-caprolactone

enaturation dipentaerythritol hexaacrylate *2 [0063] Nippon Kayaku make :

2

	実施例		比較例	
	4	5	6	1
評価項目				
現像性	○	○	○	○
現像性	○	○	○	○
感度	9	9	10	9
表面光沢	○	○	○	○
板そり	○	△	○	×
曲性	○	○	○	×
着性	○	○	○	○
筆硬度	6H	6H	6H	7H
溶剤性	○	○	○	○
酸性	○	○	○	○
熱性	○	○	○	○
金メッキ性	○	○	○	○
PCT性	○	○	○	○
熱衝撃性	○	○	○	×

0064] Even when the photopolymer constituent of this invention is high sensitivity, and the hardening film is also excellent in solder thermal resistance, chemical resistance, gold plate-proof nature, etc., a crack does not occur on a hardened material front face but the thin-film-ized substrate is used so that clearly from the result of Table 2, it is clear that it is the photopolymer constituent for printed circuit boards which does not have camber in a substrate.

0065]

Effect of the Invention] Excelling in photosensitivity in formation of the paint film by the hardened material carrying out exposure hardening by ultraviolet rays at an alkali water-solution fusibility urethane-ized epoxy carboxylate compound and the photopolymer constituent list using it, the obtained hardened material fully satisfies flexibility, adhesion, a pencil degree of hardness, solvent resistance, acid resistance, thermal resistance, gold plate-proof nature, etc., and fits the photopolymer constituent for printed wired boards especially.

Translation done.]